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Measurement and prediction of dew points of six natural gases

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ABSTRACT

Dew point measurements for six natural gases, originating from different gas fields of the Norwegian Continental Shelf, were performed using a custom made chilled mirror apparatus. The natural gas samples were taken from different points of the Norwegian pipeline network and their composition was determined by gas chromatography. The experimental dew point data cover a temperature range from 259 to 297 K and a pressure range from 12 to 110 bar. The performance of SRK, PR, PC-SAFT and UMR-PRU models has been evaluated against the experimental data. The results indicate that the best model for hydrocarbon dew point predictions, especially at high pressures and the cricondenbar pressure, is the UMR-PRU model.

1. Introduction

Accurate prediction of the hydrocarbon dew point (HCDP) of natural gases is of great importance for the oil and gas industry as it is one of the gas quality specifications used for ensuring safe transport and processing of natural gas [1]. Avoiding hydrocarbon condensation in pipelines is crucial as the presence of liquids increases the pressure drop and introduces operational problems resulting from the two phase flow in pipelines designed for single phase transportation. In the Norwegian Continental Shelf, gas pipelines are used to transport partly processed gas from offshore installations to onshore facilities in the dense phase region and thus, a cricondenbar specification has to be fulfilled. In the European pipeline system, transporting fully processed gas to the end-user, the most used dew point specification is the cricondentherm specification.

The HCDP measurements are usually directly conducted in apparati based on the chilled mirror approach, either automatic or manual. Other methods have also been mentioned but are not of common industrial practice [2–4]. Experimental HCDP data have been measured mainly for synthetic natural gases [5–12], while only a few are available in the literature for natural gases originating from gas fields, which, from this point forward, will be referred to as real natural gases. The other method used for HCDP determination is the so-called indirect method, where the HCDP is determined by combining gas chromatography (GC) for compositional analysis of the gas with a thermodynamic model for dew point calculation. Comparisons between direct and indirect methods for dew point determination have been conducted in the literature in the form of model evaluation [11–13].

One of the most important factors for accurate dew point predictions with the indirect methods is the GC analysis, as shown by Brown et al. [11] who compared dew point predictions with the same EoS but different types of GCs, for laboratory and for industrial use, and found them diverging up to 2 K, due to the inability of the process chromatograph to detect traces of heavier hydrocarbons.

The other factor is the accuracy of the thermodynamic model used for the dew point calculations. Due to their simplicity and accuracy, the most commonly used models for this purpose are cubic Equations of State (EoSs). Many variations of the original versions of the Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) EoS have been proposed over the years to improve hydrocarbon dew point predictions. The most common modification of the cubic EoSs is targeting on pure compound property predictions by modifying the temperature dependency of the attractive

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parameter, *a*, of the EoS. The underlying reason for this modification is the improvement of the description of the vapor pressures of the subcritical and therefore condensable, heavy components of natural gases and also the PVT behavior of the supercritical components, mainly methane and nitrogen, which could lead to more accurate dew point predictions for natural gases. Improvement over the original EoSs in the representation of the heavy compound vapor pressures is achieved by many researchers [14–25] while others have also focused on the supercritical behavior of the light hydrocarbons [24–29], by correlating methane fugacity coefficients, binary VLE data, Henry's constants and PVT properties in the supercritical region, thus creating families of EoSs, based on the original cubic ones.

Worth mentioning is the work of Nasrifar et al. [30,31] who evaluates different variations of the cubic EoS in the dew point prediction of natural gas mixtures and concludes that the RK family EoSs are better. Modifications of PR EoS have also been proven quite successful in the dew point predictions of natural gases, as pointed out by the work of Floter et al. [28], Saffari [23] and Haghtalab et al. [32]. Martinez and Hall [33] compare a generalized three-parameter Redlich–Kwong/Peng–Robinson (RK-PR) EoS of Cismondi and Mollerup [34] with the also three parameter Patel-Teja EoS [35], that had already been proven to be more accurate than the two parameter EoS, and concluded that the RK-PR is better for dew point predictions.

Assuming that the pure EoS parameters are accurately calculated, appropriate mixing rules are also required, for accurate dew point modeling. When the traditional van der Waals one-fluid (vdW1f) mixing rules are used, use of binary interaction parameters (BIPs) is expected to yield the optimum results, usually with some form of temperature dependency. This however is not always the case as shown by Nasrifar [31] and Louli et al. [12], who state that the use of BIPs does not necessarily improve the accuracy of the EoS in the dew point predictions of synthetic natural gases. Danesh [36] showed that the temperature independent BIPs do not change appreciably from one cubic EoS to another similar one. Moreover, since the BIPs are of empirical nature, their values are valid in specific temperature-pressure ranges in which they were correlated [1]. Correlations and predictive methods have been developed for the evaluation of BIPs [37–40]. Due to many inconsistencies in the determination of accurate BIPs, when the gases consist purely of hydrocarbons, and primarily of methane, their values are usually set to zero [29,39], while for natural gases with lower concentrations of methane and higher asymmetries, or mixtures with gases like nitrogen and carbon dioxide, their use is suggested [1]. Apart from the vdW1f mixing rules, by combination of an EoS with a local composition model, new and advanced mixing rules have also been successfully used for dew point predictions coupled with the classical EoS. The most successful ones for hydrocarbon VLE modeling found in the literature include MHV2 [41], LCVM [42], PSRK [43] and UMR-PRU [12,44]. These models are considered as purely predictive, through the incorporation of the UNIFAC method, which makes them attractive for industrial applications.

Non-cubic EoSs have also been used for dew point predictions, mainly those of the SAFT family [45]. Again, many variations of this EoS have resulted in a whole family of SAFT-based EoSs, some of which have been evaluated for dew point predictions of natural gases [46,47], with PC-SAFT [48,49] being the most popular and successful one. PC-SAFT was compared to cubic EoSs in dew point predictions in various publications [31,46,50,51]. The use of PC-SAFT is recommended by Ting et al. [46] compared to PR and other versions of SAFT in the dew point prediction of asymmetric systems. This is in accordance with Alfradique [50], who showcased that both EoSs have similar accuracy at low pressures, up to the cricondentherm point (maximum temperature of the phase envelope), while the cricondenbar point (maximum pressure of the phase envelope) was underestimated by both, with PC-SAFT being more accurate than PR.

To the best of our knowledge, the evaluation of the models presented so far in the literature for dew point predictions has been limited to synthetic mixtures. However, natural gas is a very complex mixture consisting of many compounds that cannot be fully determined by GC analysis, which poses significant challenges in the dew point predictions. The usual laboratory practice is accurate compositional analysis up to normal pentane or hexane, and grouping of the rest of the components in several fractions C6, C7, C8, C9 etc., according to their boiling point or carbon number. The available fractions depend on the limitations of the GC used for compositional analysis. Some physical properties like the molecular weight, specific gravity, density or boiling point are usually measured and the hydrocarbon type is sometimes expressed as a PNA (Parafins, Napthenes, Aromatics) composition [52].

The common industrial practice on the other hand provides only one single plus fraction, usually accompanied by its molecular weight and/or specific gravity [53]. The plus fraction is treated continuously through a distribution function [54,55], or split to subfractions by various methods, which are presented in detail by Naji [56] and Riazi [57]. For PC-SAFT, characterization methods have also been proposed by Liang [58]. Since the heavy fraction of the natural gases is very important for dew point predictions [59], it is obvious that an accurate characterization method of the plus fraction is required in order to describe the mixture as accurately as possible.

Six real natural gases (RGs) have been studied in this work. The natural gas samples are natural gases with low concentration of N_2 and CO_2 and were taken from different producing fields in the Norwegian Continental Shelf. Their composition was determined by gas chromatography using PNA characterization for the description of the C7, C8, and C9 subfractions. Hydrocarbon dew point measurements have been performed covering a temperature-range from 259 to 297 K and a pressure-range from 12 to 110 bar. Moreover, the experimental data have been used for the evaluation of the performance of SRK, PR, UMR-PRU and PC-SAFT models.

2. Experimental

2.1. Materials

The gases employed in this work are export natural gases from different fields of the Norwegian Continental Shelf (NCS). A representative sample is needed to obtain the necessary composition accuracy and this is only achievable through sampling at single phase conditions [60]. Gas samples used in this paper were taken in the dense phase area or downstream of a compressor at high temperatures. During sampling, attention has to be paid to ensure that the sample is in the single phase area. Direct sampling on an empty cylinder will cause liquid to be formed due to Joule-Thomson cooling. Piston cylinders with 1 L volume and the possibility of applying back pressure are used for sampling. Such cylinders are divided in two separate sections by a sleeve. When sampling starts, one side of the cylinder is filled with back pressure gas, usually argon, which is above the process pressure. In this way the pressure in the cylinder is maintained during sampling. Sampling starts when the back pressure is reduced slightly below the process pressure. Using this procedure, gentle sampling can be performed without risk of condensation. The typical time span for filling a 1 L cylinder is 2 min. The sample cylinders were transported to Statoil RDI laboratories in Trondheim, Norway, where the measurements were performed. All six gases contain low concentrations of